

WHAT IS CLAIMED IS:

1. An article of manufacture for dispensing a liquid adhesive, said article comprising

an applicator body,

5 a liquid adhesive contained within said applicator body,

a porous applicator tip attached to said applicator body and in a non-contacting relationship with said liquid adhesive, and

10 a first polymerization initiator or rate modifier loaded in or on said applicator tip, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium salts and tertiary amines.

2. The article of manufacture of claim 1, further comprising a frangible vial held within said applicator body, and wherein said liquid adhesive is contained within said frangible vial.

15 3. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is a tetraalkyl ammonium halide.

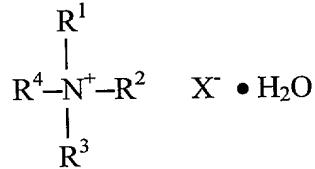
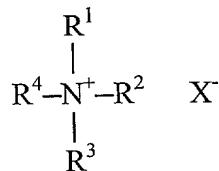
4. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is a tetrabutyl ammonium halide.

5. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is tetrabutyl ammonium chloride.

20 6. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium salts.

7. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium salts other than benzalkonium chloride.

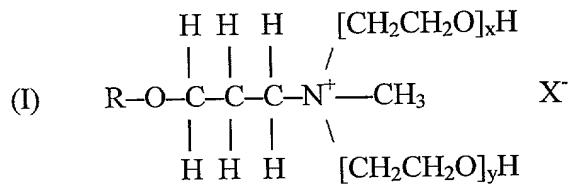
25 8. The article of manufacture of claim 7, wherein said first polymerization initiator or rate modifier is a quaternary ammonium salt represented by one of the following formula:



wherein X⁻ is selected from the group consisting of Cl⁻, F⁻, Br⁻, I⁻, SO₄²⁻, HSO₄⁻, and OH⁻; and R¹, R², R³, and R⁴ are the same or different and are selected from the group consisting of alkyl groups, aryl groups, and aralkyl groups having from 1 to about 20 carbon atoms.

5. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is an ether amine quaternary compound.

10. The article of manufacture of claim 9, wherein said ether amine quaternary compound is a compound of formula (I):



15. wherein R is a straight or branched alkyl group of from about 2 to about 20 carbon atoms, x and y independently represent an integer of from 1 to about 10, and X is a counterion.

20. 11. The article of manufacture of claim 10, wherein said counterion is selected from the group consisting of chloride, fluoride, iodide, bromide, sulfate, hydrogen sulfate, sulfite, hydrogen sulfite, bisulfite, carbonate, and bicarbonate.

25. 12. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium sulfates and quaternary ammonium bisulfates.

13. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium hydrogen sulfates and quaternary ammonium hydrogen bisulfates.

14. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tetrabutyl ammonium sulfates and tetrabutyl ammonium bisulfates.

30. 15. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tetrabutyl ammonium hydrogen sulfate and tetrabutyl ammonium hydrogen bisulfate.

16. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tertiary amines.

35. 17. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is soluble in said liquid adhesive.

18. The article of manufacture of claim 1, wherein said liquid adhesive comprises 1,1-disubstituted ethylene monomer.

19. The article of manufacture of claim 1, wherein said liquid adhesive comprises a cyanoacrylate monomer.

5 20. The article of manufacture of claim 1, wherein said liquid adhesive further comprises at least one plasticizer.

10 21. The article of manufacture of claim 20, wherein said plasticizer is selected from the group consisting of acetal trihexyl citrate, cetyl trihexyl citrate, fatty acid esters, tributyl citrate, acetyl tri-n-butyl citrate, polymethylmethacrylate, polydimethylsiloxane, and hexadimethylsilazane.

22. The article of manufacture of claim 1, wherein said first polymerization initiator or rate modifier is chemically bonded to a material forming said porous applicator tip.

15 23. The article of manufacture according to claim 22, wherein said applicator tip comprises a polymerized material.

24. The article of manufacture according to claim 22, wherein said applicator tip comprises a material selected from the group consisting of metal, glass, paper, ceramics, and cardboard.

20 25. The article of manufacture according to claim 22, wherein said applicator tip comprises a plastics material.

26. The article of manufacture according to claim 22, wherein said applicator tip is at least one of porous, absorbent and adsorbent in nature.

25 27. The article of manufacture according to claim 22, further comprising a second polymerization initiator or rate modifier loaded in or on said applicator tip, wherein said second polymerization initiator or rate modifier is different from said first polymerization initiator or rate modifier.

28. The article of manufacture according to claim 27, wherein said first and second polymerization initiator or rate modifier each initiates or modifies a rate of polymerization of said liquid adhesive.

30 29. The article of manufacture according to claim 27, wherein said second polymerization initiator or rate modifier comprises benzalkonium chloride.

30. The article of manufacture according to claim 27, wherein said second polymerization initiator or rate modifier is adsorbed or absorbed on said porous applicator tip.

31. A method of making the article of manufacture of claim 1, comprising:
loading said first polymerization initiator or rate modifier into said
porous applicator tip during manufacture of the porous applicator tip;
disposing said liquid adhesive within said applicator body; and
5 disposing said porous applicator tip at an open end of said applicator
body.

32. The method of claim 31, wherein said loading step comprises mixing
said first polymerization initiator or rate modifier with a precursor material of said
porous applicator tip.

10 33. The method of claim 32, wherein said mixing is conducted prior to
molding said porous applicator tip.

15 34. The method of claim 31, wherein said initiator is selected from the
group consisting of tetrabutylammonium bromide, sodium tetradecyl sulfate,
dodecyldimethyl(3-sulfopropyl)ammonium hydroxide, imidazole, tryptamine, urea,
arginine, povidine, phosphines, triethyl phosphite, phosphonium salts, methyl gallate,
ascorbic acid, tannic acid, sodium bisulfite, magnesium hydroxide, calcium sulfate,
sodium silicate, thiourea, polysulfides, monensin, nonactin, calixarenes, polymeric
epoxides, carbonates, cobalt naphthenate, manganese acetylacetone and phase
transfer catalysts.

20 35. The method of claim 31, wherein the first polymerization initiator or
rate modifier is selected from the group consisting of quaternary ammonium salts and
tertiary amines.

36. The method of claim 31, wherein said first polymerization initiator or
rate modifier is a tetraalkyl ammonium halide.

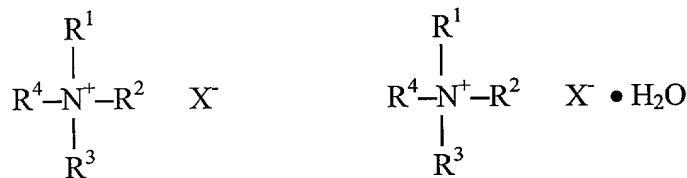
25 37. The method of claim 31, wherein said first polymerization initiator or
rate modifier is a tetrabutyl ammonium halide.

38. The method of claim 31, wherein said first polymerization initiator or
rate modifier is tetrabutyl ammonium chloride.

30 39. The method of claim 31, wherein said first polymerization initiator or
rate modifier is selected from the group consisting of quaternary ammonium salts.

40. The method of claim 39, wherein said first polymerization initiator or
rate modifier is a quaternary ammonium salt represented by one of the following
formula:

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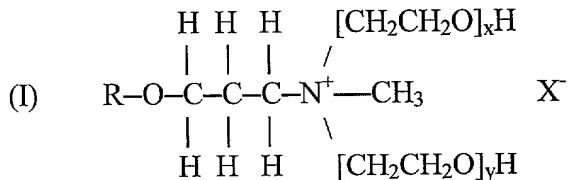
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wherein X^- is selected from the group consisting of Cl^- , F^- , Br^- , I^- , SO_4^{2-} , HSO_4^- , and OH^- ; and R^1 , R^2 , R^3 , and R^4 are the same or different and are selected from the group consisting of alkyl groups, aryl groups, and aralkyl groups having from 1 to about 20 carbon atoms.

41. The method of claim 31, wherein said first polymerization initiator or rate modifier is an ether amine quaternary compound.

42. The method of claim 41, wherein said ether amine quaternary compound is a compound of formula (I):

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wherein R is a straight or branched alkyl group of from about 2 to about 20 carbon atoms, x and y independently represent an integer of from 1 to about 10, and X is a counterion.

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43. The method of claim 42, wherein said counterion is selected from the group consisting of chloride, fluoride, iodide, bromide, sulfate, hydrogen sulfate, sulfite, hydrogen sulfite, bisulfite, carbonate, and bicarbonate.

44. The method of claim 31, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium sulfates and quaternary ammonium bisulfates.

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45. The method of claim 31, wherein said first polymerization initiator or rate modifier is selected from the group consisting of quaternary ammonium hydrogen sulfates and quaternary ammonium hydrogen bisulfates.

46. The method of claim 31, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tetrabutyl ammonium sulfates and tetrabutyl ammonium bisulfates.

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47. The method of claim 31, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tetrabutyl ammonium hydrogen sulfate and tetrabutyl ammonium hydrogen bisulfate.

48. The method of claim 31, wherein said first polymerization initiator or rate modifier is selected from the group consisting of tertiary amines.

49. The method of claim 31, wherein said first polymerization initiator or rate modifier is soluble in said liquid adhesive.

5 50. The method of claim 31, wherein said first polymerization initiator or rate modifier is chemically bonded to a material forming said porous applicator tip.

51. The method of claim 50, wherein said applicator tip comprises a polymerized material.

10 52. The method of claim 50, wherein said applicator tip comprises a material selected from the group consisting of metal, glass, paper, ceramics, and cardboard.

53. The method of claim 50, wherein said applicator tip comprises a plastics material.

15 54. The method of claim 50, wherein said applicator tip is at least one of porous, absorbent and adsorbent in nature.

55. The method of claim 50, further comprising loading a second polymerization initiator or rate modifier in or on said applicator tip subsequent to manufacture of said applicator tip, wherein said second polymerization initiator or rate modifier is different from said first polymerization initiator or rate modifier.

20 56. The method of claim 55, wherein said first and second polymerization initiator or rate modifier each initiates or modifies a rate of polymerization of said liquid adhesive.

57. The method of claim 55, wherein said second polymerization initiator or rate modifier comprises benzalkonium chloride.

25 58. The method of claim 55, wherein said second polymerization initiator or rate modifier is adsorbed or absorbed on said porous applicator tip.

59. The method of claim 31, wherein said loading step comprises:
mixing said first polymerization initiator or rate modifier with pellets of a polymeric material; and

30 molding said mixture to form said porous applicator tip.

60. The method of claim 31, wherein said loading step comprises mixing said first polymerization initiator or rate modifier with pellets of a polymeric material while molding said pellets to form said porous applicator tip.

61. The method of claim 31, wherein said loading step comprises:
forming said porous applicator tip in a mold; and
applying said first polymerization initiator or rate modifier to said mold
as a release agent, in an amount sufficient for said first polymerization initiator or rate
modifier to be loaded in or on said porous applicator tip.
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62. The method of claim 31, wherein said loading step comprises:
mixing said first polymerization initiator or rate modifier with foam
precursor materials; and
forming a foam from said foam precursor materials to form said porous
10 applicator tip.
63. The method of claim 31, wherein said loading step comprises mixing
said first polymerization initiator or rate modifier with a foam material while blowing
or expanding said foam material, to form said porous applicator tip.
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64. The method of claim 31, wherein said first polymerization initiator or
rate modifier is not substantially decomposed during said loading step.
65. An article of manufacture for dispensing a liquid adhesive, said article
comprising
20 an applicator body,
a liquid adhesive contained within said applicator body,
a porous applicator tip attached to said applicator body and in a non-
contacting relationship with said liquid adhesive, and
an exchange resin that functions as at least one of a stabilizer or as a
polymerization initiator or rate modifier for said liquid adhesive.
66. The article of manufacture of claim 65, wherein said exchange resin is
25 a polymerization initiator or rate modifier for said liquid adhesive.
67. The article of manufacture of claim 65, wherein said exchange resin is
a stabilizer for said liquid adhesive.
68. The article of manufacture of claim 65, wherein said exchange resin is
in a form of particles or beads.
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69. The article of manufacture of claim 65, wherein said exchange resin is
mixed with or dispersed in said liquid adhesive.
70. The article of manufacture of claim 65, wherein said exchange resin is
located in said applicator body in a non-contacting relationship with said liquid
adhesive.

71. The article of manufacture of claim 65, wherein said exchange resin is located in or on said porous applicator tip.

72. An article of manufacture for dispensing a liquid adhesive, said article comprising

5 an applicator body,

a liquid adhesive and a phase transfer catalyst contained within said applicator body, and

10 a porous applicator tip attached to said applicator body and through which said liquid adhesive is dispensed.

73. The article of manufacture of claim 72, further comprising a frangible vial held within said applicator body, and wherein said liquid adhesive and phase transfer catalyst are contained within said frangible vial.

15 74. The article of manufacture of claim 72, wherein said phase transfer catalyst is selected from the group consisting of quaternary ammonium sulfates and quaternary ammonium bisulfates.

75. The article of manufacture of claim 72, wherein said phase transfer catalyst is selected from the group consisting of quaternary ammonium hydrogen sulfates and quaternary ammonium hydrogen bisulfates.

20 76. The article of manufacture of claim 72, wherein said phase transfer catalyst is selected from the group consisting of tetrabutyl ammonium sulfates and tetrabutyl ammonium bisulfates.

77. The article of manufacture of claim 72, wherein said phase transfer catalyst is selected from the group consisting of tetrabutyl ammonium hydrogen sulfate and tetrabutyl ammonium hydrogen bisulfate.

25 78. The article of manufacture of claim 72, wherein said liquid adhesive comprises 1,1-disubstituted ethylene monomer.

79. The article of manufacture of claim 72, wherein said liquid adhesive comprises a cyanoacrylate monomer.

30 80. The article of manufacture of claim 72, wherein said phase transfer catalyst is a direct initiator for said liquid adhesive following a nucleophilic substitution reaction of said phase transfer catalyst and a stronger nucleophilic group.

81. The article of manufacture of claim 72, wherein said nucleophilic substitution reaction replaces a sulfate or bisulfate group in said phase transfer catalyst.

82. The article of manufacture of claim 72, further comprising a polymerization initiator or rate modifier loaded in or on said applicator tip.

83. The article of manufacture of claim 82, wherein said polymerization initiator or rate modifier is different from said phase transfer catalyst.

5 84. The article of manufacture of claim 82, wherein said polymerization initiator or rate modifier initiates or modifies a rate of polymerization of said liquid adhesive.

85. The article of manufacture of claim 82, wherein said polymerization initiator or rate modifier comprises benzalkonium chloride.

10 86. The article of manufacture of claim 82, wherein said polymerization initiator or rate modifier is adsorbed or absorbed on said porous applicator tip.

87. a polymerizable monomer adhesive composition, comprising:

a 1,1-disubstituted ethylene monomer;

an anionic stabilizing agent for said 1,1-disubstituted ethylene

15 monomer; and

a phase transfer catalyst.

88. The composition of claim 87, wherein said phase transfer catalyst is selected from the group consisting of quaternary ammonium sulfates and quaternary ammonium bisulfates.

20 89. The composition of claim 87, wherein said phase transfer catalyst is selected from the group consisting of quaternary ammonium hydrogen sulfates and quaternary ammonium hydrogen bisulfates.

90. The composition of claim 87, wherein said phase transfer catalyst is selected from the group consisting of tetrabutyl ammonium sulfates and tetrabutyl 25 ammonium bisulfates.

91. The composition of claim 87, wherein said phase transfer catalyst is selected from the group consisting of tetrabutyl ammonium hydrogen sulfate and tetrabutyl ammonium hydrogen bisulfate.

92. The composition of claim 87, wherein said liquid adhesive comprises a 30 cyanoacrylate monomer.

93. The composition of claim 87, wherein said phase transfer catalyst is a direct initiator for said liquid adhesive following a nucleophilic substitution reaction of said phase transfer catalyst and a stronger nucleophilic group.

94. The composition of claim 87, wherein said nucleophilic substitution reaction replaces a sulfate or bisulfate group in said phase transfer catalyst.

95. The composition of claim 87, wherein said phase transfer catalyst also acts as a stabilizer for said 1,1-disubstituted ethylene monomer.